

# PATENT SPECIFICATION

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## (54) ZIRCONIUM PHOSPHATE PRODUCT

(71) We, CCI LIFE SYSTEMS, INC. a corporation of the State of Delaware, of 16601 Saticoy Street, Van Nuys, State of California 91406, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to zirconium phosphate products and their use in ion exchangers.

The use of hydrous oxide ion exchangers for separating inorganic ions from an aqueous solution has been investigated and results are reported in U.S. Patent No. 3,332,737. In the terminology of this patent, a zirconium hydrous oxide ion exchanger is defined as amorphous or microcrystalline solids containing zirconium or zirconium plus other oxides or hydroxides and varying amounts of water, with exchangeable ions depending on the substances and their treatment. Although such material may be described by a particular formula or name, it should be understood that these materials have no simple or definite stoichiometric composition and may not have any crystal structure when examined by X-ray diffraction.

Zirconium phosphate ion exchangers have been prepared by mixing together a solution of zirconium compound and a solution of a phosphate. The resulting precipitate material is either a very fine powder or a gelatinous insoluble material suspended in an aqueous solution. These products are very difficult to filter to remove water and require a substantial amount of equipment to accomplish the filtration of a very small amount of zirconium phosphate. When a gelatinous material results, the material after filtration is dried and is comprised of large, hard particles.

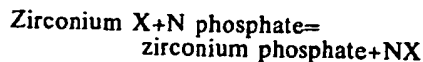
When fine zirconium phosphate is produced by reacting an aqueous solution of a zirconium salt with an aqueous solution of a phosphate, the resulting product may

be a mixed phosphate of non-stoichiometric composition, containing cations from the soluble phosphate. Aqueous solutions are used because homogeneous reactions tend to go to completion and are more rapid. The fine powder resulting after filtering and drying is too fine to be utilized in an ion exchanger column because the resistance to flow through the column is too great.

Larger crystalline zirconium phosphate can be produced as set forth in United States Patent No. 3,416,884. The solutions are boiled for several days and microscopic or non-crystalline substances are converted slowly into macroscopic crystalline zirconium phosphate. However, the time involved in the heating process makes this product expensive. Because of the difficulties in producing granular zirconium phosphate with present methods, the product has not been used extensively.

The present invention provides a process for the production of a zirconium phosphate product in particulate form which comprises incorporating particles of a water-soluble zirconium compound into an aqueous phosphate solution having a molar concentration of at least 0.5, allowing said zirconium compound to react with said phosphate and recovering the particulate zirconium phosphate product so formed.

The general reaction for the conversion of zirconium starting compound into zirconium phosphate in accordance with the present invention is as follows:



Where X is an anion of a soluble zirconium starting compound and N is a cation of soluble phosphate.

The mechanism of reaction is that the phosphate in the soluble phosphate solution is exchanged for the anion in the soluble zirconium compound. The zirconium phosphate, being insoluble, fixes the zirconium in the configuration found when the phosphate contacts it.

In practice, the phosphate solution with the zirconium compound particles added is stirred for a period from five to thirty minutes to ensure that the phosphate ions penetrate into the inside of the zirconium compound particles, thereby converting substantially all of the zirconium compound into an insoluble zirconium phosphate. The solution is then filtered free of the reaction mixture and washed with water until all soluble phosphate is removed. Thereafter, to ensure that there is sufficient phosphate penetration under given production conditions, the granules can be tested to determine if there is free zirconium compound left in them. The process may conveniently be carried out at any temperature between room temperature and 100°C. The zirconium starting compound must be sufficiently soluble for chemical exchange with the phosphate to occur and should be at least slightly more soluble than the resulting zirconium phosphate product. Amongst suitable materials there may be mentioned, for example, zirconium oxychloride, zirconium nitrate, zirconium sulphate, zirconium acetate and basic zirconium sulphate.

The final particle size of the zirconium phosphate product is controlled by the particle size of the zirconium starting compound, and if, for example, a 1 millimeter piece of zirconium oxychloride is used as the starting compound, the final particles of zirconium phosphate will be slightly larger than 1 millimeter. In general, the final particle size increases slightly but there is some introduction of finer particles because of the processing of the particles. It has been determined that the use of starting particles greater than 12 mesh results in granules that are very weak physically and can be crushed easily in subsequent operations. Also, it has been determined that starting particles smaller than 325 mesh produce granules which are too fine for filtration is present in any substantial amount. Generally speaking, therefore, size should be in the 12 to 325 mesh distribution band with the majority of the particles being of intermediate size.

The concentration of the phosphate solution preferably remains above 0.5 molar throughout the reaction in order to prevent the formation of a product which can too easily be broken down to undesired very fine particles. It follows, therefore, that the phosphate used should be sufficiently soluble for such a concentration to be obtained. Thus semi-soluble compounds such as calcium phosphate are unsuitable.

Amongst preferred materials there may be mentioned, for example, phosphoric acid, sodium phosphate and a mixed

sodium hydrogen phosphate. With most materials the initial concentration can go to the solubility limit but with phosphoric acid the concentration is preferably kept below 2.5 molar to avoid the formation of a gelled product.

The process of the present invention is especially applicable to methods of producing zirconium phosphate ion exchangers in any desired mesh size range. The process is particularly useful for making a granular product in a mesh size range suitable for use in ion exchange columns for liquids from which inorganic ions are to be separated. Present requirements for such ion exchangers exist in the treatment of dialysis solution for artificial kidney systems to remove the ammonia resulting from the conversion of urea by urease. Such a treatment is disclosed in United States Patent No. 3,669,880. In this system, the ammonium ion resulting from the conversion of urea is removed by a zirconium phosphate ion exchanger in a column and the phosphate in the dialysis solution returning from the artificial kidney is removed by a hydrous zirconium oxide ion exchanger. The dialysis provides a recirculating flow process in which the dialysis fluid returning from the kidney is continuously passed through a column or columns containing granular zirconium phosphate and hydrous zirconium oxide.

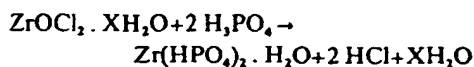
It has been determined that zirconium phosphate particles in the 12 to 325 mesh distribution band may be used in the exchanger column provided that there is not a substantially large amount of 325 mesh particles nor an excessively large amount of 12 mesh particles (all references to mesh size herein are to Tyler standard screen scale sieve size). The finer mesh material inhibits the flow of liquid and tends to pack in the column, even though the liquid makes good contact with the material. On the other hand, the large particles permit easy flow through the column but do not allow sufficient surface area of zirconium compound to be exposed to the liquid in order to pick up the ions.

The process of the present invention can readily be used to produce zirconium phosphate in this desired mesh size range, because the initial mesh of the particles of the soluble zirconium starting compound determines the mesh distribution band of the zirconium phosphate product, the starting compound being converted into zirconium phosphate without dissolving in the phosphate solution and without substantial disintegration or weakening of the particles.

The following Examples illustrate the invention.

## EXAMPLE 1

One preferred process for the production of zirconium phosphate is the reaction of zirconium oxychloride with phosphoric acid as exemplified by the following reaction:



Where X is normally 0 to 8

The form of the final zirconium phosphate product is a mixed compound in which the zirconium phosphate is only a part of the product; the product has no known fixed chemical formula.

In such a process 49.5 grams zirconium oxychloride screened 28—48 mesh was slowly added to a stirred solution of 100 ml concentrated phosphoric acid dissolved in 900 ml of water, the granular product was filtered, washed, and air-dried. Initial molar concentration of phosphate was 1.4 and final mesh was 20—80.

## EXAMPLE 2

30 grams zirconium basic sulphate 200—325 mesh was slowly added to a stirred 20 ml concentrated phosphoric acid dissolved in 180 ml of water. The product was filtered, washed, and air-dried. Initial molar concentration of phosphate was 1.4 and final mesh was 150—325.

## EXAMPLE 3

17.7 grams zirconium oxychloride screened 20—150 mesh was slowly added to a stirred solution of 69 grams sodium dihydrogen phosphate mono hydrate dissolved in 500 ml water. The product was filtered, washed and air-dried. Initial molar concentration of phosphate was 1.0 and final mesh was 16—200.

## EXAMPLE 4

10 grams zirconyl nitrate (glass) screened 14 mesh and above were slowly added to a stirred solution of 20 cc concentrated phosphoric acid in 180 cc of water. The product was filtered, washed, and air-dried. Initial molar concentration was 1.4 and final mesh was 12 or greater.

## EXAMPLE 5

17 grams zirconium oxychloride screened 28—48 mesh was slowly added to a stirred solution of 35 ml concentrated phosphoric acid dissolved in 965 ml of water. The granular product was filtered, washed and air-dried. Initial molar concentration of phosphate was 0.5 and final mesh was 10—325.

The final molar concentration of phosphate was less than 0.5 molar and the

product was unsatisfactory for column use because the large particles easily broke into dust, giving particles of smaller mesh than 325.

## EXAMPLE 6

120 grams zirconium oxychloride screened 28—48 mesh was slowly added to a stirred solution of 100 ml concentrated phosphoric acid dissolved in 900 ml of water. The granular product was filtered, washed, and air-dried. Initial phosphate molar concentration was 1.4 and final mesh was 12—80. The final molar concentration of phosphate was 0.5.

## EXAMPLE 7

49.5 grams zirconium oxychloride screened 28—48 mesh was slowly added to a stirred solution of 170 ml concentrated phosphoric acid dissolved in 830 ml of water. The granular product was filtered, washed and air-dried. Initial molar concentration of phosphate was 2.5 and final mesh was 28—60.

## EXAMPLE 8

32 pounds zirconium oxychloride screened 14 mesh and above was slowly added to a stirred solution of 3.2 gallons 75% phosphoric acid dissolved in 24 gallons of water. The finished product was filtered, washed and air-dried. The initial molar concentration of phosphate was 1.5 and final mesh was 12 and above.

In the above Examples, the molar concentration at all times exceeded 0.5 except for Example 5 where a product was produced which was unsatisfactory for column use. In the case of Example 7, the initial molar concentration of phosphate was 2.5 which was found to be the approximate upper limit for this particular phosphate compound. Example 8 is typical of a commercial production run wherein approximately 40 pounds of product was produced.

From the above description, it is apparent that the phosphate solution can fix the zirconium in insoluble form in substantially the particle configuration found when the reagent contacts it. Thus, the resulting granular size is within substantially the same range as the initial granular size and this permits the mesh distribution band of the final product to be determined by the initial mesh band. Also, the final product can be commercially produced in a band of particle size which is acceptable in a typical ion exchange column.

Thus it will be seen that the present invention provides a low-cost, commercially feasible process for preparing zirconium phosphate in granular form

5 suitable for use in ion exchanger type  
columns, especially in dialysis methods and  
in water treatment apparatus. The resulting  
granular product forms rapidly so that long  
and expensive filtration is not required and  
the product lends itself to high production  
quantities. It will be appreciated, however,  
that the process is also applicable to the  
10 production of larger particles, which can  
later be crushed to a suitable size, if  
desired, and also to the production of very  
fine particles, which are useful in other  
applications, because the final particle size  
is dependent on the initial size of the  
15 particles of the zirconium starting material.

WHAT WE CLAIM IS:—

1. A process for the production of a  
zirconium phosphate product in particulate  
form which comprises incorporating  
20 particles of a water-soluble zirconium  
compound into an aqueous phosphate  
solution having a molar concentration of at  
least 0.5, allowing said zirconium  
compound to react with said phosphate and  
recovering the particulate zirconium  
25 phosphate product so formed.

2. A process as claimed in claim 1,  
wherein the particles of the zirconium  
starting compound have a size range similar  
30 to that of ion exchanger particles suitable  
for use in an ion exchange column.

3. A process as claimed in claim 1 or  
claim 2, wherein the particle size range of  
the zirconium starting compound is from 12  
35 to 325 mesh.

4. A process as claimed in any one of  
claims 1 to 3, wherein the zirconium  
starting compound is zirconium  
40 oxychloride.

5. A process as claimed in any one of  
claims 1 to 3, wherein the zirconium  
starting compound is zirconium basic  
sulphate.

6. A process as claimed in any one of  
45 claims 1 to 3, wherein the zirconium

starting compound is zirconium nitrate,  
zirconium sulphate or zirconium acetate.

7. A process as claimed in any one of  
claims 1 to 6, wherein the phosphate is  
50 sodium phosphate, a mixed sodium hydrogen  
phosphate, or phosphoric acid.

8. A process as claimed in any one of  
claims 1 to 7, wherein the temperature lies  
in the range of from room temperature to  
55 100°C.

9. A process as claimed in any one of  
claims 1 to 8, wherein the particles of the  
zirconium starting compound are added to  
the aqueous phosphate solution with stirring  
which is continued.  
60

10. A process as claimed in claim 9,  
wherein stirring is continued for from 5 to  
30 minutes.

11. A process as claimed in any one of  
claims 1 to 10, wherein the particulate  
zirconium phosphate product is recovered  
by filtration.  
65

12. A process as claimed in any one of  
claims 1 to 11, wherein the recovered  
zirconium phosphate product is washed  
with water after separation from the  
70 solution.

13. A process as claimed in claim 1,  
carried out substantially as described in any  
one of the Examples herein.  
75

14. A particulate zirconium phosphate  
product whenever prepared by a process as  
claimed in any one of claims 1 to 13.

15. An ion-exchange column or water  
treatment apparatus which contains a  
particulate zirconium phosphate product as  
claimed in claim 14.  
80

16. A dialysis method which uses an ion-  
exchange column as claimed in claim 15.

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